

High C/O Chemistry and Weak Thermal Inversion in the Extremely Irradiated Atmosphere of Exoplanet WASP-12b

Nikku Madhusudhan¹, Joseph Harrington², Kevin B. Stevenson², Sarah Nymeyer², Christopher J. Campo², Peter J. Wheatley³, Drake Deming⁴, Jasmina Blečić², Ryan A. Hardy², Nate B. Lust², David R. Anderson⁵, Andrew Collier-Cameron⁶, Christopher B. T. Britt², William C. Bowman², Leslie Hebb⁷, Coel Hellier⁴, Pierre F. L. Maxted⁴, Don Pollacco⁸, Richard G. West⁹

¹ *Kavli Institute for Astrophysics and Space Research, and Department of Earth, Atmospheric, and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, MA 02139, USA.* ² *Planetary Sciences Group, Department of Physics, University of Central Florida, Orlando, FL 32816-2385, USA.* ³ *Department of Physics, University of Warwick, Coventry, CV4 7AL, UK.* ⁴ *NASA's Goddard Space Flight Center, Greenbelt, MD 20771-0001, USA.* ⁵ *Astrophysics Group, Keele University, Staffordshire ST5 5BG, UK.* ⁶ *School of Physics and Astronomy, University of St. Andrews, North Haugh, Fife KY16 9SS, UK* ⁷ *Department of Physics and Astronomy, Vanderbilt University, Nashville, TN 37235, USA.* ⁸ *Astrophysics Research Centre, School of Mathematics & Physics, Queen's University, University Road, Belfast, BT7 1NN, UK.* ⁹ *Department of Physics and Astronomy, University of Leicester, Leicester, LE1 7RH, UK*

The carbon-to-oxygen ratio (C/O) in a planet provides critical information about its primordial origins and subsequent evolution. A primordial C/O greater than 0.8 causes a carbide-dominated interior as opposed to the silicate-dominated composition as found on Earth¹; the solar C/O is 0.54². Theory shows that high C/O leads to a diversity of carbon-rich planets that can have very different interiors and atmospheres from those in the solar system^{1,3}. Here we report the

detection of $C/O \geq 1$ in a planetary atmosphere. The transiting hot Jupiter WASP-12b⁴ has a dayside atmosphere depleted in water vapour and enhanced in methane by over two orders of magnitude compared to a solar-abundance chemical equilibrium model at the expected temperatures. The observed concentrations of the prominent molecules^{5,6} CO, CH₄, and H₂O are consistent with theoretical expectations for an atmosphere with the observed $C/O = 1$. The C/O ratios are not known for giant planets in the solar system, although they are expected to equal the solar value^{7,8}. If high C/O ratios are common, then extrasolar planets are likely very different in interior composition, and formed very differently, from expectations based on solar composition^{1,3,8}, potentially explaining the large diversity in observed radii. We also find that the extremely irradiated atmosphere (> 2500 K) of WASP-12b lacks a prominent thermal inversion, or a stratosphere, and has very efficient day-night energy circulation. The absence of a strong thermal inversion is in stark contrast to theoretical predictions for the most highly irradiated hot-Jupiter atmospheres^{9,10,11}.

The transiting hot Jupiter WASP-12b orbits a star slightly hotter than the Sun (6300 K) in a circular orbit at a distance of only 0.023 AU, making it one of the hottest exoplanets known⁴. Thermal emission from the dayside atmosphere of WASP-12b has been reported using the Spitzer Space Telescope¹², at 3.6, 4.5, 5.8, and 8 μm ¹³ wavelengths, and from ground-based observations in the J (1.2 μm), H (1.6 μm), and Ks (2.1 μm) bands¹⁴ (Figure 1).

The observations provide constraints on the dayside atmospheric composition and thermal structure, based on the dominant opacity source in each bandpass. The J, H, and Ks channels¹⁴ do not have significant molecular absorption features, and hence probe the deepest layers of the observable atmosphere, at pressure (P) of ~ 1 bar, where the temperature (T) is ~ 3000 K (Figure 1). The Spitzer observations¹³, on the other hand,

are excellent probes of molecular composition. CH_4 has strong absorption features in the 3.6 μm and 8 μm channels, CO has strong absorption in the 4.5 μm channel, and H_2O has its strongest feature in the 5.8 μm channel and weaker features in the 3.6 μm , 4.5 μm , and 8 μm channels. The low brightness temperatures in the 3.6 μm (2700 K) and 4.5 μm (2500 K) channels, therefore, clearly suggest strong absorption due to CH_4 and CO, respectively. The high brightness temperature in the 5.8 μm channel, on the other hand, indicates low absorption due to H_2O . The strong CO absorption in the 4.5 μm channel also indicates temperature decreasing with altitude, since a thermal inversion would cause emission features of CO in the same channel with a significantly higher flux than at 3.6 μm ^{6,16}.

The broadband observations allow us to infer the chemical composition and temperature structure of the dayside atmosphere of WASP-12b, using a statistical retrieval technique⁶. We combined a 1-D atmosphere model with a Markov-chain Monte Carlo sampler^{6,17} that computes over 4×10^6 models to explore the parameter space. The phase space included thermal profiles with and without inversions, and equilibrium and non-equilibrium chemistry over a wide range of atomic abundances. Our models include the dominant sources of infrared opacity in the temperature regime of WASP-12b^{5,18,19}: H_2O , CO, CH_4 , CO_2 , $\text{H}_2 - \text{H}_2$ collision induced absorption, and TiO and VO where the temperatures are high enough for them to exist in gas phase^{9,20}. The host star has a significantly enhanced metallicity ($2 \times \text{solar}$)⁴, and evolutionary processes can further enhance the abundances^{7,8}; Jupiter has $3 \times \text{solar}$ C/H (Ref. 7). Our models therefore explore wide abundance ranges: $\sim 0.05 - 100 \times \text{solar}$ for C/H and O/H, and $0.1 - 10 \times \text{solar}$ for C/O. Figure 2 shows the mixing ratios of H_2O , CO, CH_4 , and CO_2 , and the ratios of C/H, O/H and C/O, required by the models at different levels of fit. Figure 3 presents the temperature profiles.

We find a surprising lack of water and overabundance of methane (Figure 2). At 2000 – 3000 K, assuming solar abundances yields CO and H₂O as the dominant species besides H₂ and He^{19,20}. Most of the carbon, and the same amount of oxygen, are present in CO, and some carbon exists as CH₄. The remaining oxygen in a hydrogen-dominated atmosphere is mostly in H₂O; small amounts are also present in species such as CO₂. The CO/H₂ and H₂O/H₂ mixing ratios should each be $> 5 \times 10^{-4}$, CH₄/H₂ should be $< 10^{-8}$, and CO₂/H₂ should be $\sim 10^{-8}$, under equilibrium conditions at a nominal pressure of 0.1 bar. The requirement of $\text{H}_2\text{O}/\text{H}_2 \leq 8 \times 10^{-6}$ and $\text{CH}_4/\text{H}_2 \geq 4 \times 10^{-6}$ (both at 3σ significance; Figure 2) is therefore inconsistent with equilibrium chemistry using solar abundances.

The observations place a strict constraint on the C/O ratio. We detect a $\text{C/O} > 1$ at 3σ significance (Figure 2). Our results rule out a solar C/O of 0.54 at 4.4σ . Our calculations of equilibrium chemistry with a C/O ratio of 1 yield mixing ratios of H₂O, CO and CH₄ that are consistent with the observed constraints. We find that, for $\text{C/O} = 1$, H₂O mixing ratios as low as 10^{-7} and CH₄ mixing ratios as high as 10^{-5} can be attained in the 0.1 – 1 bar level for temperatures around 2000 K and higher. And, while the CO mixing ratio is predicted to be $> 10^{-4}$, making it the dominant molecule after H₂ and He, CO₂ is predicted to be negligible ($< 10^{-9}$). These theoretical predictions for a C/O = 1 atmosphere, are consistent with the observed constraints on H₂O, CH₄, CO, and CO₂ (Figure 2).

The observations rule out a strong thermal inversion deeper than 0.01 bar (Figure 3). Thermal inversions at lower pressures have opacities too low to induce features in the emission spectrum that are resolvable with current instruments. For comparison, all stratospheric inversions in solar system giant planets, and those consistent with hot Jupiter observations, exist at pressures between 0.01 – 1 bar^{6,16,21}. The major contributions to all the observations come from the lower layers of the atmosphere, $P >$

0.01 bar, where we rule out a thermal inversion (Figure 1 of SI). The observations also suggest very efficient day-night energy redistribution (Figure 2). The low brightness temperatures at 3.6 and 4.5 μm imply that only part of the incident stellar energy is reradiated from the dayside, while up to 45% is absorbed and redistributed to the nightside. The possibility of a deep thermal inversion and inefficient redistribution was suggested recently¹⁴, based on observations in the J, H, and Ks channels, but the Spitzer observations rule out both conditions.

The lack of a prominent thermal inversion contrasts existing theories, which designate WASP-12b to the class of very hot Jupiters which are expected to host inversions^{9,22}. At $T > 2000\text{K}$, molecules such as TiO and VO, which are strong absorbers in the UV/visible, are expected to be gas phase and potentially cause thermal inversions⁹. WASP-12b therefore presents a major challenge to existing atmospheric classification schemes for exoplanets based on thermal inversions^{9,22}. However, it remains to be seen if the high continuum UV flux expected for WASP-12b might be efficient in photo-dissociating inversion-causing compounds in the atmosphere thus explaining the lack of a strong inversion¹⁰. Alternatively, the present result might support theories which suggest that TiO and VO are less likely to be present aloft in the atmosphere to cause thermal inversions²⁰.

If high C/O ratios are common, then the formation processes and compositions of extrasolar planets are likely very different from expectations based on solar system planets. The host star has enhanced metallicity but the C/O ratio is unknown^{4,23,24}. In the core accretion model, favoured for the formation of Jupiter, icy planetesimals containing heavy elements coalesce to form the core, followed by gas accretion^{8,25}. The abundances of elemental oxygen and carbon are enhanced equally^{7,8}, maintaining a C/O like the star's. The host star WASP-12 is thus expected to have a C/O ~ 1 . If the stellar C/O is independently determined to be < 1 , then the C/O enhancement in WASP-12b's

atmosphere would suggest either an unusual origin for the planetesimals, a local over-density of carbonaceous grains^{3,26}, or a different formation mechanism entirely. Although carbon-rich giant planets like WASP-12b have not been studied, theoretical studies predict myriad compositions for carbon-dominated solid planets^{1,3}. Terrestrial-sized carbon planets, for instance, could be dominated by graphite or diamond interiors, as opposed to the silicate composition of Earth^{1,3}. In the context of hot Jupiters, a dominance of carbon among the heavy elements in the interiors would likely change the mass and radius estimates from what have been calculated, based on solar abundances.

The observed molecular abundances in the dayside atmosphere of WASP-12b motivate a new regime in atmospheric chemistry. It remains to be seen if photochemistry in WASP-12b can significantly alter the composition in the lower layers of the atmosphere, $P = 0.1 - 1$ bar, which contribute most to the observed spectrum (Figure 1 of SI). Explaining the observed composition as a result of photochemistry with solar abundances would still be challenging. CH_4 is more readily photo-dissociated compared to H_2O ^{11,27}, and hence a depletion of CH_4 over that predicted with solar abundances might be expected, as opposed to the observed enhancement of CH_4 . Apart from the spectroscopically dominant molecules considered in this work, other species such as OH, C_2H_2 , and FeH (Refs. 27, 28), which are not detectable by current observations, could potentially be detected with high-resolution spectra in the future. Most models of exoplanetary atmospheres have typically assumed solar abundances and/or solar C/O, thereby exploring a very limited region of parameter space^{9,16,29}. The case of WASP-12b is a strong motivation for models to depart from solar abundances and abundance ratios.

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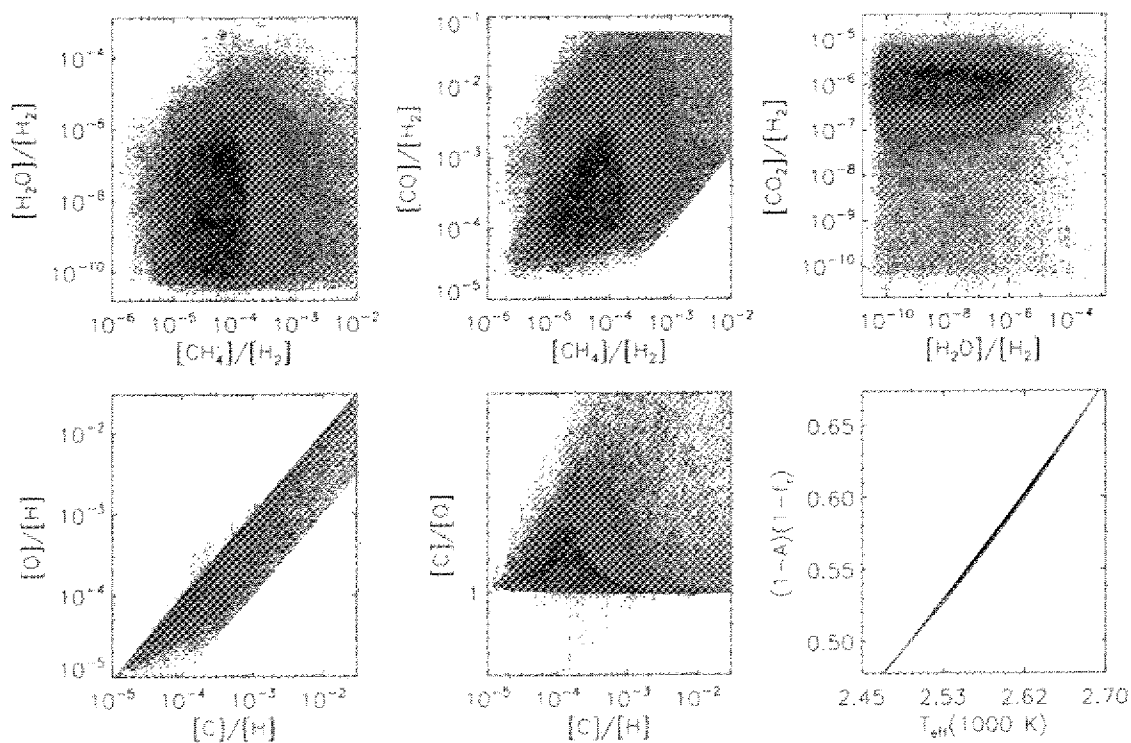
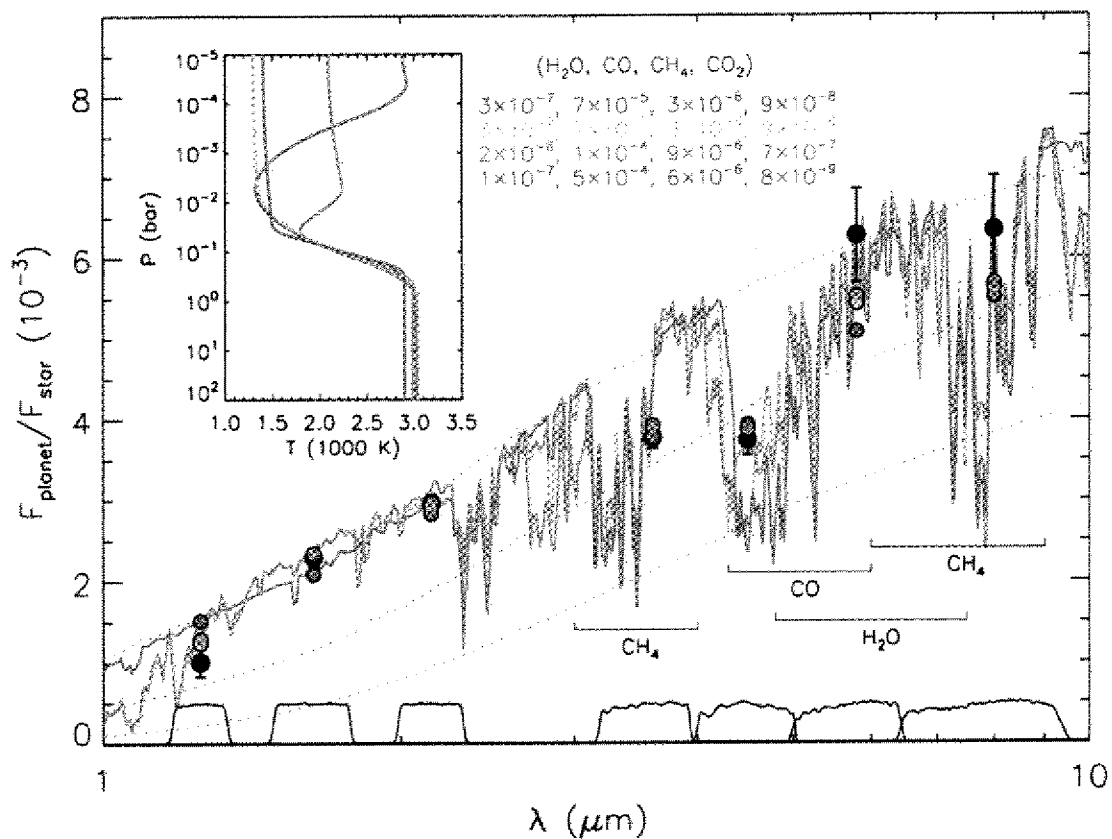
Author Information: Correspondence and requests for materials should be addressed to N.M. (e-mail: nmadhu@mit.edu).

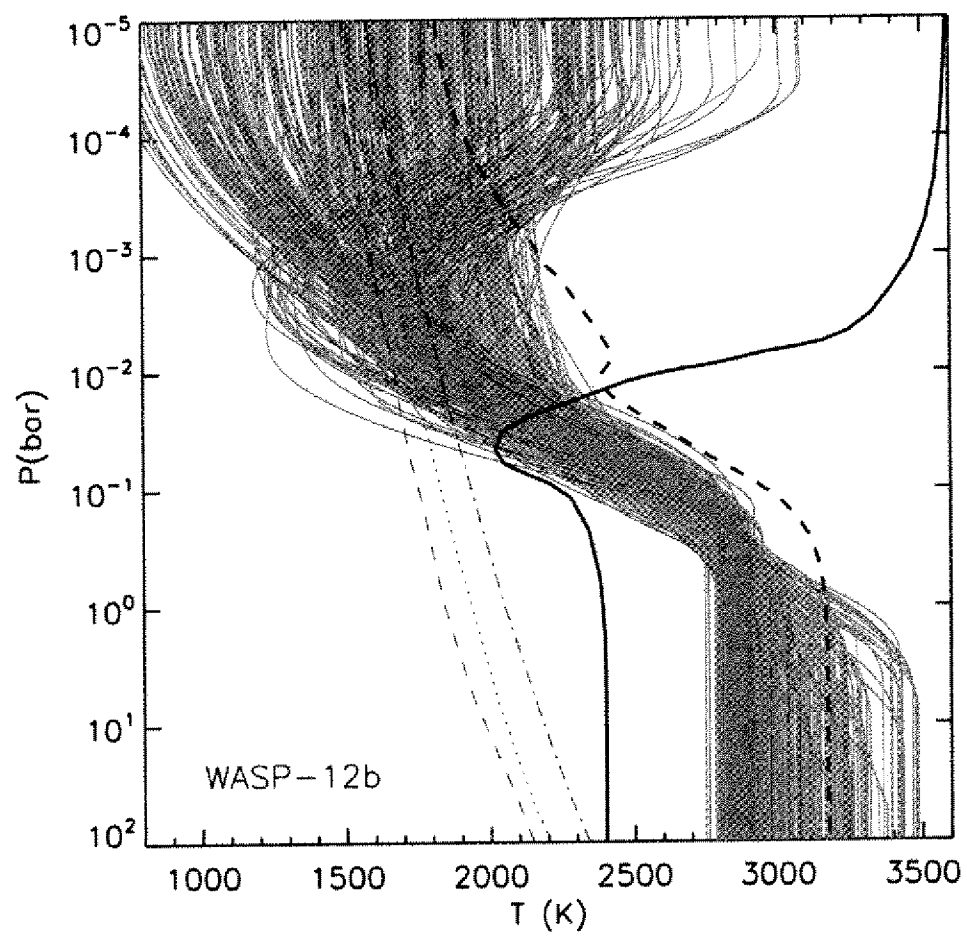
Figure 1: Observations and model spectra for dayside thermal emission of WASP-12b. The black filled circles with error bars show the data: four Spitzer observations¹³ (3.6 μm , 4.5 μm , 5.8 μm , and 8 μm ; see Table 1), and three ground-based observations in the J (1.2 μm), H (1.6 μm), and Ks (2.1 μm) bands¹⁴. Four models fitting the observations are shown in the coloured solid curves in main panel, and the coloured circles are the channel-integrated model points. The corresponding temperature profiles are shown in the inset. The molecular compositions are shown as number ratio with respect to molecular hydrogen; all the models have C/O ~ 1 . The thin gray dotted lines show blackbody spectra of WASP-12b at 2000 K (bottom), 2500 K and 3000 K (top). A Kurucz model³⁰ was used for the stellar spectrum, assuming uniform illumination over the planetary disk (i.e weighted by 0.5; Ref 10). The black solid lines at the bottom show the photometric bandpasses in arbitrary units. The low fluxes at 3.6 and 4.5 μm are explained by methane and CO absorption, respectively, required for all fitting models. The high flux in the 5.8 μm channel indicates less absorption due to H₂O. The observations can be explained to high precision by models without thermal inversions. Models with strong thermal inversions are ruled out by the data (see Figure 3). The red model features a thermal inversion at low pressures ($P < 0.01$ bar), but the corresponding spectrum is almost indistinguishable from the orange model, which has identical composition, and identical thermal profile below the 0.01 bar level as the red

model, but does not have a thermal inversion above the 0.01 bar level. Thus, any potential thermal inversion is too weak to be detectable by current instruments.

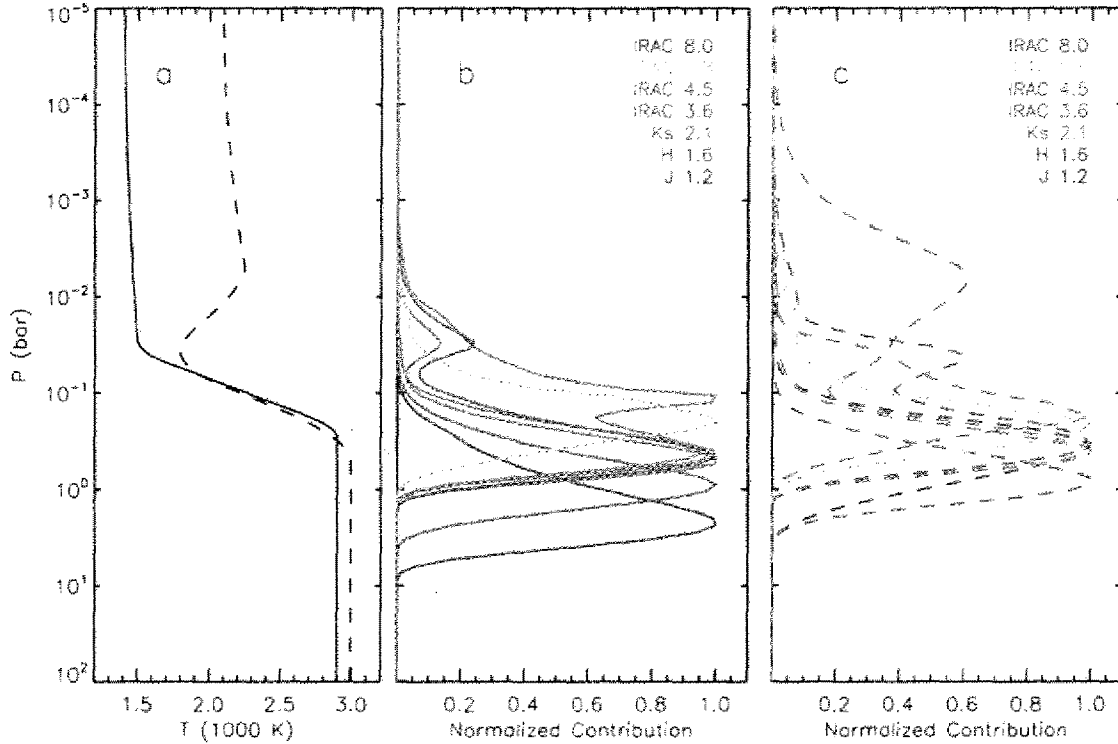
Figure 2: Constraints on the atmospheric composition of WASP-12b. The distributions of models fitting the 7 observations (Figure 1) at different levels of χ^2 are shown. The coloured dots show χ^2 surfaces, with each dot representing a model realization. The purple, red, green, and blue colours correspond to models with χ^2 less than 7, 14, 21, and 28, respectively. Mixing ratios are shown as ratios by number with respect to H_2 . At 3σ significance, the constraints on the composition are $\text{H}_2\text{O}/\text{H}_2 \leq 8 \times 10^{-6}$, $\text{CH}_4/\text{H}_2 \geq 4 \times 10^{-6}$, $\text{CO}/\text{H}_2 \geq 9 \times 10^{-5}$, $\text{CO}_2/\text{H}_2 \leq 5 \times 10^{-6}$, and $\text{C}/\text{O} > 1$. The compositions of the best-fitting models (with $\chi^2 < 7$) span $\text{H}_2\text{O}/\text{H}_2 = 10^{-10} - 10^{-6}$, $\text{CO}/\text{H}_2 = 10^{-5} - 10^{-3}$, $\text{CH}_4/\text{H}_2 = 8 \times 10^{-6} - 2 \times 10^{-4}$, and $\text{CO}_2/\text{H}_2 = 5 \times 10^{-7} - 5 \times 10^{-6}$; the corresponding ranges in the elemental abundances are $\text{C}/\text{O} = 1 - 2.5$, $\text{C}/\text{H} = 10^{-5} - 10^{-3}$ and $\text{O}/\text{H} = 10^{-5} - 10^{-3}$. The solutions with the lowest C/H and O/H ratios correspond directly to the lowest CO abundance. Based on thermo-chemical equilibrium, the inferred CH_4/H_2 and $\text{H}_2\text{O}/\text{H}_2$ mixing ratios are possible only for $\text{C}/\text{O} \geq 1$, consistent with our detection of $\text{C}/\text{O} \geq 1$. The last panel shows the constraints on the day-night energy redistribution, given by $(1-A)(1-f_r)$, where 'A' is the bond albedo and ' f_r ' is the fraction of incident energy redistributed to the night side. Up to $f_r = 0.45$ is possible (for $A = 0$). Thus, the observations support very efficient redistribution. An additional observation in the z' (0.9 μm) band was reported recently¹⁵. However, the observation implies a value for the orbital eccentricity inconsistent with other data in the literature^{13, 14}. We therefore decided to exclude this observation from the analysis presented here, although including it does not affect our conclusions regarding the value of C/O or the temperature structure.

Figure 3: Thermal profiles of WASP-12b. The purple, red, green, and orange profiles correspond to models that fit the observations to within χ^2 of 7, 14, 21, and 28, respectively (same models as in Figure 2); only 100 randomly chosen profiles for each χ^2 level are shown, for clarity. The thick, black, solid (dashed) curve shows a published profile from a self-consistent model of WASP-12b with (without) a thermal inversion, adapted from Ref. 20, which assumes solar abundances. If a thermal inversion is present in WASP-12b, it is expected to be prominent, as shown by the solid black curve. A prominent thermal inversion between 0.01 – 1 bar is ruled out by the data at 4σ . The ostensibly large inversions in the figure are at low pressures (below 0.01 bar), which have low optical depths, and hence minimal influence on the emergent spectrum (see Figure 1). The observations are completely consistent with thermal profiles having no inversions. Small thermal inversions are also admissible by the data, and could potentially result from dynamics. The thin dotted, dashed, and dash-dot lines in black show condensation curves of TiO at solar, $0.1 \times$ solar, and $10 \times$ solar composition²⁰.





Supplementary Information



SI Figure 1: Contribution functions for representative WASP-12b models showing the atmospheric origin of flux observed in each bandpass. Two representative temperature profiles are shown in panel a (same as the purple and green profiles of Figure 1). The contribution functions in panel b (panel c) correspond to the solid (dashed) temperature profile in panel a, colour-coded by bandpass. The maximum contribution to the emergent flux of WASP-12b in all the channels comes from the lowest layers of the observable atmosphere, below the 0.1 bar level.